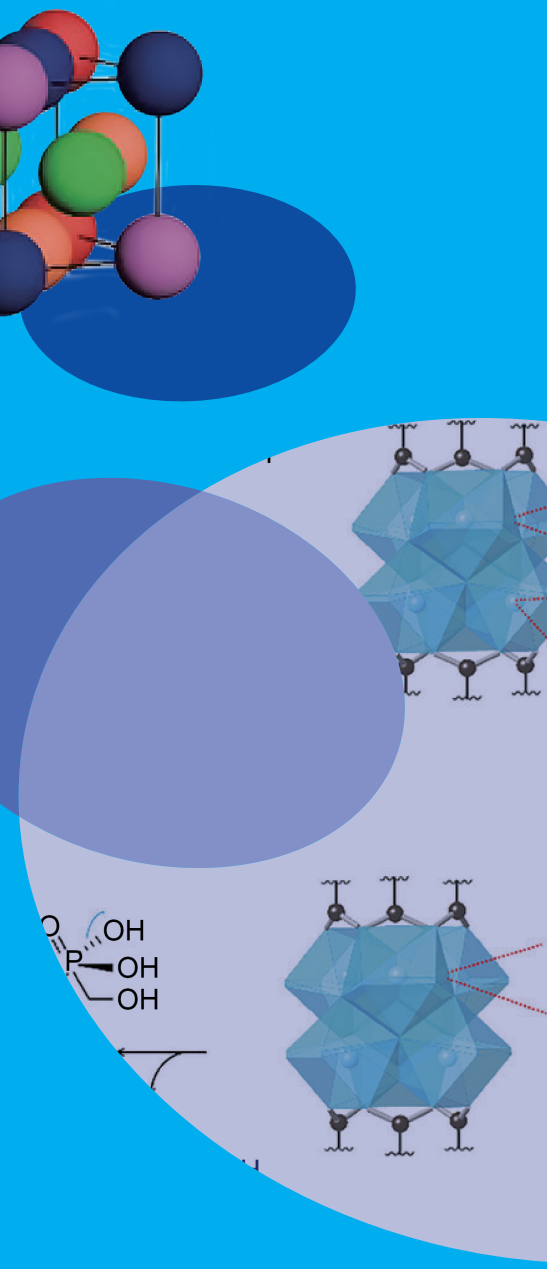
Chemical Science



Chemical science is at the core of synchrotron research, where advances in photon-based techniques continually redefine how we observe, understand, and design matter at atomic and molecular levels. Contemporary chemical research increasingly addresses complex, interdisciplinary challenges—such as sustainable energy conversion, environmental remediation, advanced functional materials, and soft electronics—that cannot be resolved through conventional characterization methods alone. In this context, synchrotron radiation has become an indispensable tool, enabling scientists to directly probe chemical structures, electronic states, and dynamic processes under realistic conditions.

This section highlights representative studies that demonstrate how synchrotron-based methods—including X-ray diffraction (XRD), X-ray absorption spectroscopy (XAS), extended X-ray absorption fine structure (EXAFS), grazing-incidence wide-angle X-ray scattering (GIWAXS), and advanced X-ray imaging—provide critical insights into contemporary chemical problems. Collectively, these studies showcase the breadth of chemical research supported by synchrotron facilities, spanning hard and soft matter, molecular catalysis, nanomaterials, and environmental chemistry.

A central theme of this section is the importance of atomic-level structure–function relationships. Whether investigating dopant incorporation in magic-sized semiconductor nanoclusters, catalytic active sites in metal–organic frameworks, charge transport pathways in conjugated polymers, or interfacial chemistry in high-entropy alloys and molecular catalysts, synchrotron techniques enable researchers to resolve subtle structural motifs and coordination environments that govern macroscopic properties. In many cases, features such as weak metal–oxygen bonding, dynamic coordination changes, or short-range molecular ordering are inaccessible to laboratory-based techniques but become evident through synchrotron measurements.

Another unifying aspect of the reported studies is the focus on *operando* and *in situ* characterization. Chemical systems are rarely static: catalysts restructure during reactions, polymers reorganize under mechanical strain, and redox-active materials evolve under applied potentials or thermal stress. By enabling real-time observation under working conditions, synchrotron experiments bridge the gap between idealized models and real-world chemical behavior. This capability is essential not only for fundamental understanding but also for the rational design of materials with enhanced efficiency, stability, and functionality.

The studies featured in this section reflect the increasing importance of chemical science in addressing global challenges. From degrading persistent environmental pollutants and converting greenhouse gases into valuable chemicals to designing stretchable electronics and efficient electrocatalysts based on earth-abundant elements, these works demonstrate how fundamental chemical insights lead to practical solutions.

Taken together, the NSRRC serves as a vital platform for translational research, promoting collaboration among chemists, materials scientists, physicists, and engineers. By probing matter at various length and time scales, synchrotron radiation techniques enhance our understanding of chemical phenomena and drive innovation toward a more sustainable and technologically advanced future. (by Yu-Jong Wu)

A New Twist in the World of Magic-Sized Clusters

The origin of the giant magnetic moments in Mn^{2+}-doped CdSe nanoclusters was elucidated through synchrotron X-ray diffraction and EXAFS spectroscopy.

In the evolving field of nanoscience, "magic-sized clusters" (MSC) occupy a fascinating niche between molecules and bulk solids. These ultra-small aggregates, typically less than two nanometers in diameter, exhibit discrete energy levels and unique quantum properties that cannot be explained by classical semiconductor physics. Among them, $(CdSe)_{13}$ nanoclusters have become a model system for understanding how atomic-scale surface chemistry dictates optoelectronic behavior. A collaborative team led by Elise Yu-Tzu Li and Yi-Hsin Liu from National Taiwan Normal University uncovered an unexpected phenomenon: Mn^{2+}-doped $(CdSe)_{13}$ nanoclusters exhibit an extraordinary magnetic moment exceeding 40 μB at 180 K, which is nearly an order of magnitude larger than expected for such diluted magnetic systems.[1]

One of the most challenging questions in nanotechnology is how dopant atoms integrate into nanoclusters. In bulk or even quantum-dot materials, doping mechanisms can often be modeled statistically. However, in MSCs, where each cluster contains only a few dozen atoms, every dopant counts. The local environment of a single Mn^{2+} ion can drastically alter the entire system's electronic and magnetic responses depending on its coordination number, bonding partners, and surrounding ligands. Synchrotron-based extended X-ray absorption fine structure (EXAFS) at the Cd K-edge and Mn K-edge provided crucial insights. By analyzing the oscillations in X-ray absorption beyond the edge, EXAFS allowed the researchers to quantitatively determine interatomic distances, coordination numbers, and the presence of specific bonding shells (Cd–Se, Cd–N, Cd–O, Mn–O, and Mn–N) with sub-angstrom precision. The EXAFS measurements performed at **TLS 01C2** and **TLS 17C1** revealed that clusters synthesized from two different selenium precursors exhibited strikingly different coordination environments, as shown in **Fig. 1**. In Se–urea-derived clusters, Cd atoms were coordinated mainly by Se and N atoms (Cd–Se ≈ 2.62 Å, Cd–N ≈ 2.36 Å). By contrast, Se–$NaBH_4$-derived clusters required an additional Cd–O shell at 2.35 Å to fit the EXAFS data accurately. This subtle but crucial difference signaled that oxygen atoms from acetate ligands were directly bonded to Cd, forming mixed Cd–O and Cd–N coordination networks. X-ray diffraction (XRD) measurements performed at **TPS 09A** and **TLS 01C1** further reveal that Mn^{2+} doping is markedly more efficient in the Se–$NaBH_4$–derived $(CdSe)_{13}$ nanoclusters, which contain Cd–O and Mn–O coordination, than in those prepared from Se–urea, where Cd–O bonding is absent. The Se–$NaBH_4$ route yields dopant concentrations nearly an order of magnitude higher, demonstrating a substantially enhanced incorporation of Mn^{2+}. Such bonding motifs could not be inferred from optical or NMR data alone; they emerged clearly only through synchrotron EXAFS analysis. The presence of Cd–O bonding turned out to be the missing piece of the puzzle. In Se–$NaBH_4$-derived clusters, acetate ligands introduced oxygen atoms capable of forming strong Cd–O and Mn–O bonds, thus stabilizing the tetrahedral Mn^{2+} coordination within the cluster core. This chemical environment dramatically enhanced the dopant incorporation efficiency, raising Mn^{2+} substitution levels to over 12%, compared to just 1.3% in Se–urea-derived samples that lacked Cd–O interactions.

With the structure clarified, the researchers could now interpret the unexpected magnetic and optical phenomena. Mn^{2+}-doped $(CdSe)_{13}$ clusters synthesized *via* the Se–$NaBH_4$ route exhibited a fivefold increase in photoluminescence (PL) intensity, along with prolonged emission lifetimes and field-dependent blue shifts in PL spectra under magnetic fields up to 0.5 T. These magneto-optical effects originated from spin–spin coupling between Mn^{2+} ions and photoexcited carriers within the quantum-

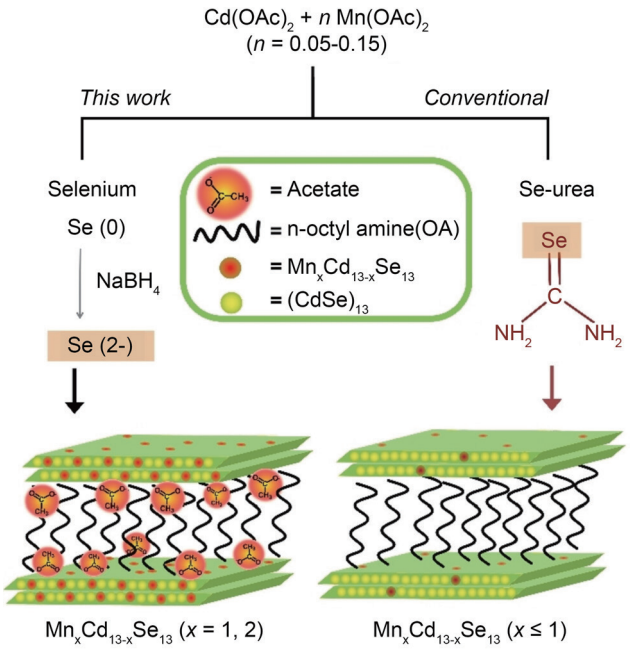


Fig. 1: Schematic representation of synthetic processes with the two selenium-based precursors, Se-$NaBH_4$ and Se-urea, employed in this study. [Reproduced from Ref. 1]

confined clusters. Density functional theory calculations revealed that transitions between ferromagnetic and antiferromagnetic states correspond to energies around 1.9–2.0 eV, which match the experimental PL emission near 600 nm. Interestingly, at low dopant levels (< 1%), the PL blue-shifted under magnetic fields, implying magnetic-field-induced destabilization of spin-coupled excitonic recombination. At higher dopant concentrations (~6–7%), excessive spin–spin coupling quenched PL, owing to nonradiative recombination *via* dark exciton states. These results paint a complex but coherent picture: surface ligand chemistry dictates local coordination of the dopant, which in turn governs spin exchange, exciton dynamics, and magneto-optical behavior.

Magnetic measurements performed using a superconducting quantum interference device magnetometer revealed that Mn^{2+}-doped $(CdSe)_{13}$ nanoclusters display paramagnetism with a hint of ferromagnetic hysteresis at 2 K. More astonishingly, the effective magnetic moment reached over 40 μB per cluster at 180 K, vastly exceeding the theoretical spin-only contribution (5.5 μB) of isolated Mn^{2+} ions. The researchers proposed a mechanism involving charge redistribution and spin fluctuations at the Se-rich cluster surfaces. Mulliken population analyses indicated electron transfer from the amine ligands to Se atoms through Cd, creating localized charge imbalances and unpaired spins. These surface states could couple with the Mn^{2+} spins to form magnetic polarons, where charge carriers and localized spins align collectively under internal magnetic fields up to 30 T. Such dynamic spin alignment and electron precession within the clusters explain the enhanced magnetic susceptibility and the emergence of giant magnetic moments. The interplay of ligand chemistry, spin–orbit coupling, and magnetic polaron formation defines a new paradigm for magnetically active nanomaterials that function even at relatively high temperatures. (Reported by Yu-Jong Wu)

This report features the work of Elise Yu-Tzu Li, Yi-Hsin Liu and their collaborators published in Angew. Chem. Int. Ed. ***64****, e202420257 (2025).*

TPS 09A Temporally Coherent X-ray Diffraction
TLS 01C2 X-ray Powder Diffraction
- XRD
- Materials science

TLS 01C1 EXAFS
TLS 17C1 EXAFS
- EXAFS
- Materials sciences

Reference

1. G.-L. Huang, K.-Y. Ting, N. Narayanam, D.-R. Wu, T.-E. Hsieh, K.-C. Tsai, D.-W. Yang, Q.-X. Tang, B.-K. Su, Y.-T. Kang, S.-J. Huang, C.-H. Chen, Y.-P. Chang, L.-S. Yang, Y.-C. Chao, E. Y.-T. Li, Y.-H. Liu, Angew. Chem. Int. Ed. **64**, e202420257 (2025).

Atomic-Level Recycling of a Controversial Herbicide

Through combined experimental and synchrotron analyses, this work reveals the mechanism by which MOF-808 degrades glyphosate and converts it into non-toxic species.

Glyphosate (N-phosphonomethyl glycine; GPh), one of the most widely used herbicides globally, has faced increasing scrutiny for its persistence in ecosystems and potential health impacts. Traditional remediation strategies, such as microbial degradation or oxidation, often transform GPh into equally problematic byproducts like aminomethyl phosphonic acid (AMPA) or phosphoric acid, both of which can be toxic or contribute to eutrophication. The pressing challenge has been to develop a catalytic process that decomposes GPh into truly benign products under mild, environmentally friendly conditions.

A recent study by a collaborative team from the University of New South Wales (Australia), Universidad Nacional de Córdoba (Argentina), Colorado School of Mines (USA), and the NSRRC discovered that Zr-based metal–organic framework nanocrystals (nMOF-808) can completely degrade GPh at room temperature, producing N-formyl glycine and hydroxymethyl phosphonate with very low toxicity.[1] Most remarkably, the reaction proceeds without external energy input and leaves no harmful residues in solution, as the phosphonate byproduct remains bound to the catalyst framework.

MOF-808 is a zirconium-based porous framework consisting of $Zr_6O_4(OH)_4$ clusters connected by benzene-1,3,5-tricarboxylate linkers. Its high stability in water and tunable coordination environment make it ideal for catalytic reactions involving polar molecules. The research team synthesized MOF-808 in two crystal sizes to examine the role of surface defects

and coordinatively unsaturated sites. The nanocrystalline version (nMOF-808) exhibited remarkably enhanced catalytic activity, achieving 95% GPh degradation in just two hours at room temperature, compared to 72% for larger crystals. Nuclear magnetic resonance and mass spectrometry confirmed the production of N-formyl glycine, a benign amino acid derivative, rather than toxic AMPA. Moreover, the catalyst remained effective after multiple reaction cycles, demonstrating robust reusability.

A central question was why the smaller crystals performed considerably better. To address this, the team employed synchrotron-based X-ray absorption spectroscopy (XAS), including extended X-ray absorption fine structure (EXAFS) and near-edge X-ray absorption fine structure. These techniques, performed at the **TPS 44A** quick-scanning XAS beamline of the NSRRC, the Australian Synchrotron, and PETRA III, provided atomic-scale insights into the local coordination environment around the Zr clusters—the catalytic "hot spots" where GPh molecules interact and decompose. EXAFS analyses revealed that at the Zr L_3- and K-edges, the zirconium centers in nMOF-808 have a higher coordination number of labile hydroxyl (–OH) and formate ligands compared to larger MOF-808 crystals. These weakly bound species are key to promoting ligand exchange with GPh, enabling the Cβ–N bond to cleave and drive the degradation reaction, as shown in **Fig. 1**. After catalysis, new scattering paths corresponding to Zr–O–P linkages were observed, confirming that phosphonate fragments become coordinated to the Zr nodes.

Through a synergy of nanostructured catalyst design and state-of-the-art synchrotron spectroscopy, the team demonstrated that zirconium-based MOF-808 nanocrystals can efficiently and selectively degrade GPh into innocuous compounds. The ligand exchange and coordination changes that drive this reaction demonstrate that the path to cleaner chemistry often begins with understanding matter at the atomic scale. This research presents an elegant proof-of-concept for transforming a controversial agrochemical into harmless substances under ambient conditions. The combination of rational catalyst design and synchrotron-enabled structural analysis paves the way for new materials capable of degrading other persistent organic pollutants safely and selectively. Beyond its immediate environmental relevance, the study also demonstrates how *in situ* synchrotron spectroscopy can reveal the dynamic chemistry of MOFs, offering a blueprint for designing next-generation catalysts for green chemistry, water purification, and environmental remediation. (Reported by Yu-Jong Wu)

This report features the work of Alejandro M. Fracaroli, Nicholas M. Bedford and their co-workers published in Angew. Chem. Int. Ed. ***64****, e202424540 (2025).*

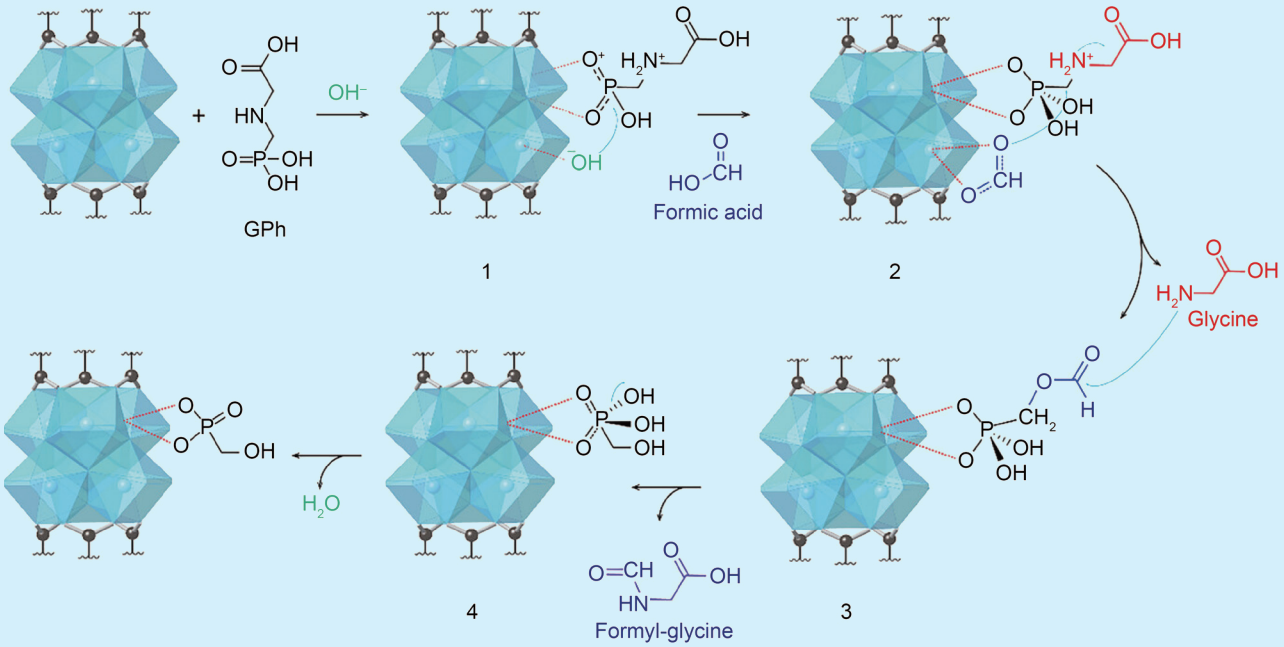


Fig. 1: Proposed degradation mechanism for GPh using MOF-808 as a heterogeneous catalyst. 1) Ligand exchange initiation: GPh's phosphonate group displaces weakly bound formate ligands from the Zr secondary building units, anchoring the molecule to the MOF surface. 2) Cβ–N bond cleavage: hydroxyl groups coordinated to Zr assist a nucleophilic attack on the Cβ atom, breaking the C–N bond to yield glycine and a formyl ester intermediate. 3) Intramolecular formylation: the amine group of glycine reacts with the formyl ester, creating N-formyl glycine. 4) Product trapping and regeneration: the remaining hydroxymethyl phosphonate binds to Zr as a new ligand, while the formate reservoir within the MOF enables multiple reaction cycles. [Reproduced from Ref. 1]

TPS 44A Quick-scanning X-ray Absorption Spectroscopy

- XAS
- Heterogeneous Catalysis, Metal–organic Frameworks

Reference

1. J. A. Peña Prada, T. A. Huertas Navarro, S. L. Chua, A. M. Granados, C.-W. Pao, A. M. Fracaroli, N. M. Bedford, Angew. Chem. Int. Ed. **64**, e202424540 (2025).

How Subtle Atomic Asymmetry Makes Polymers Both Stretchable and Electrically Fast

Through a dipole-tailored polymer design, high stretchability and fast charge transport are achieved for soft, high-performance electronic materials.

Flexible and wearable electronic devices that can stretch, bend, and conform to human skin are rapidly advancing the frontier of biomedical sensing and human–machine interfaces. However, designing polymers that are both mechanically stretchable and electronically conductive has remained a challenge. Typically, increasing flexibility tends to reduce crystalline order, which in turn slows down charge transport. A research team led by Chien-Chung Shih at National Yunlin University of Science and Technology has now addressed this dilemma through smart molecular design. Their study introduces a "dipole-tailoring strategy" that decouples polymer aggregation from crystallinity, allowing a single material to be soft, strong, and electronically agile.[1]

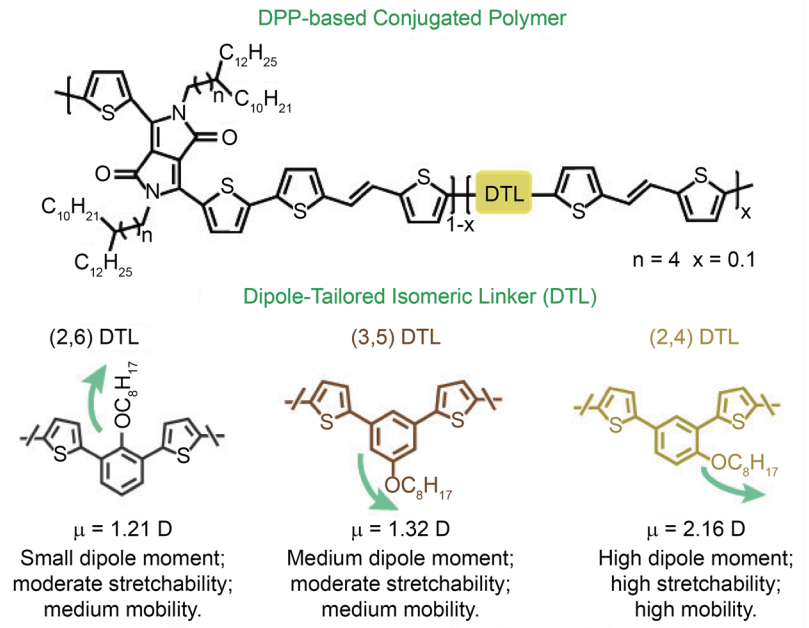


Fig. 1: Chemical structures of the DPP-based conjugated polymers and their isomeric linkers. The parent polymer backbone incorporates a DPP unit and thiophene spacers, while the DTL modulates the local dipole moment through positional variation of the alkoxy substituent on the benzene ring. The three isomers—(2,6)-DTL, (3,5)-DTL, and (2,4)-DTL—exhibit increasing dipole moments (μ = 1.21, 1.32, and 2.16 D, respectively), corresponding to progressively enhanced chain polarity and electrostatic interactions. This dipole engineering enables tunable mechanical and electronic properties: higher dipole moments lead to greater stretchability and improved charge mobility, as demonstrated in the 2,4-DTL polymer. [Reproduced from Ref. 1]

The key innovation lies in dipole-tailored isomeric linkers (DTL) that subtly rearrange the position of an alkoxy group on a benzene ring. By shifting this group from the 2,6- and 3,5- positions to the asymmetric 2,4- position, the researchers created polymers with progressively stronger internal dipoles. This seemingly minor atomic change dramatically reshapes how polymer chains pack, aggregate, and respond to mechanical stress. Through a series of carefully controlled syntheses, the team incorporated each DTL isomer into a diketopyrrolopyrrole (DPP)–thiophene polymer backbone. Spectroscopic and computational analyses showed that the asymmetric 2,4-DTL possesses the highest dipole moment (2.16 D) and the most distorted geometry, thus promoting local electrostatic attraction between chains.

To confirm how these dipolar modifications affect molecular organization, the team relied heavily on synchrotron-based grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements. GIWAXS is uniquely suited to probing the nanometer-scale order

of thin polymer films, revealing how chains stack, twist, and crystallize. Using this high-flux synchrotron X-ray technique, the team discovered that long-range crystallinity decreased as the dipole moment increased, reducing rigid lamellar domains that normally limit flexibility. In addition, short-range aggregation was enhanced, forming compact local clusters that preserve efficient π–π charge transport. The synchrotron GIWAXS data confirmed that these improvements arise not from conventional crystallization but from dipole-induced local ordering.

After establishing the structural origin of flexibility, the team demonstrated real-world device performance. When blended with a non-fullerene acceptor (Y7), PDPP-(2,4)-DTL formed a stretchable bulk-heterojunction photodiode that exhibited the following key parameters: an external quantum efficiency of 45%, detectivity (D*) exceeding 10^{12} Jones, stable operation even under 80% mechanical strain, and retention of photoresponse after 1000 stretching cycles. These results mark a breakthrough for skin-compatible optoelectronics, such as wearable heart-rate sensors, pulse oximeters, and biomedical photoplethysmography (PPG) systems. Indeed, the team demonstrated a working on-skin PPG sensor capable of recording human pulse signals in real time without any degradation under repeated bending.

By merging molecular dipole design with synchrotron X-ray characterization, the research team achieved what was long thought to be contradictory: polymers that are simultaneously soft like skin and conductive like silicon. This study establishes a new principle in polymer science: dipole engineering can be used to control local aggregation independently of long-range order, breaking the long-standing trade-off between electrical performance and mechanical stretchability. Their findings open new possibilities for stretchable transistors, photodiodes, and biomedical sensors, redefining how we design materials for the next era of flexible electronics. (Reported by Yu-Jong Wu)

This report features the work of Chien-Chung Shih and his co-workers published in J. Am. Chem. Soc. ***147****, 29282 (2025).*

TLS 13A1 X-ray Scattering

- GIWAXS
- Materials Science, Soft matters

Reference

1. C.-C. Kang, T.-M. Hung, S.-T. Lu, T.-C. Lu, C.-C. Shih, J. Am. Chem. Soc. **147**, 29282 (2025).

Turning Nitrate Waste into Useful Ammonia Fertilizer: Custom-Built Copper Molecules for Clean Catalysis

A team developed enhanced activity and selectivity of molecular Cu (I) catalysts for electrocatalytic nitrate reduction reaction (NO_3RR) by incorporating electrically charged prosthetic groups on catenane ligands.

A research team led by Ho Yu Au-Yeung and Edmund Tse at the University of Hong Kong (HKU, China) has developed a new family of copper-based molecular catalysts.[1] These catalysts efficiently convert harmful nitrate pollutants in water into valuable ammonia fertilizers. The discovery, made at the HKU–CAS Joint Laboratory on New Materials, demonstrates that precisely designed molecular structures called catenanes can enhance the selectivity and durability of catalysts used in green chemistry (**Fig. 1**).

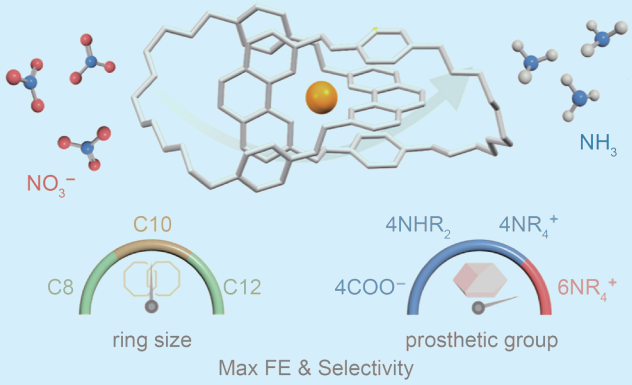


Fig. 1: Influence of prosthetic groups in Cu(I) catenane complexes and the size of interlocked macrocycles in the entangled ligands on NO_3RR. [Reproduced from Ref. 1]

Nitrate contamination from agricultural runoff, industrial discharge, and household wastewater is one of the world's most pressing water-quality problems. Traditional removal techniques often consume excessive energy and generate unwanted by-products. Converting nitrate back into ammonia provides a sustainable alternative. Ammonia is a valuable fertilizer and a potential hydrogen carrier. However, developing a low-cost, non-precious metal catalyst that can convert nitrate selectively and efficiently without causing side reactions remains a challenge.

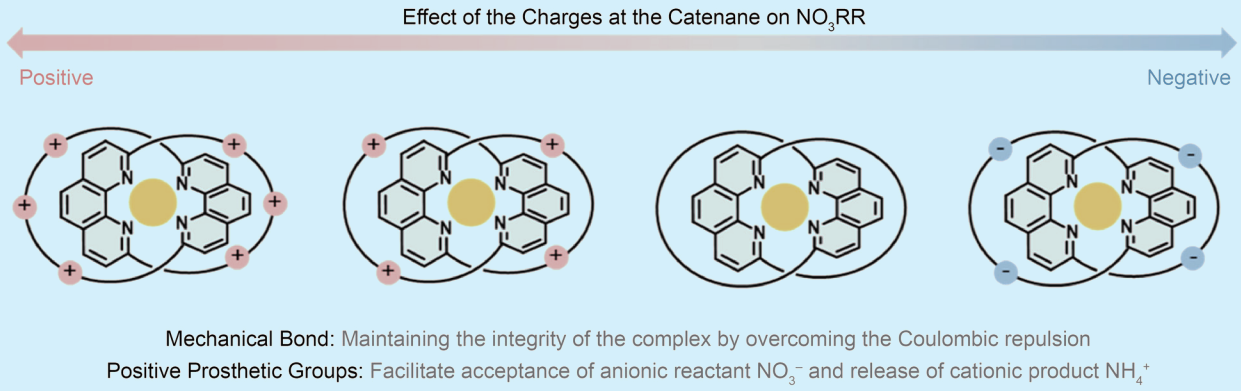


Fig. 2: Effect of prosthetic groups of the Cu(I) catenane complexes on NO_3RR. [Reproduced from Ref. 1]

Au-Yeung and Tse addressed this challenge by designing a new set of mechanically interlocked Cu(I) complexes, known as catenanes. These structures resemble tiny molecular links—two or more rings intertwined—enabling precise control over metal atom interactions during reactions. Although copper (Cu) is an abundant and affordable metal for catalysis, conventional copper catalysts often face the "activity-selectivity-durability trilemma": they may work quickly, but lack selectivity and degrade rapidly. The HKU researchers overcame this limitation by mechanically locking and chemically tuning the copper environment to create stable and highly selective catalysts.

Their approach combined two strategies:

- Mechanical Interlocking: using catenane ligands to secure the copper center, preventing unwanted structural changes during reactions.
- Covalent Modification: attaching positively charged groups to enhance attraction to negatively charged nitrate ions and facilitate the release of the positively charged ammonia product.

In the new catalysts, the copper center is positioned within an interlocked framework that resists distortion under reaction conditions. The charged groups on the catenane backbone help attract nitrate ions to the copper site, allowing electrons and protons to transfer efficiently (**Fig. 2**). According to the researchers, this design achieves two goals: it increases the conversion rate from nitrate to ammonia and reduces competing reactions, such as unwanted hydrogen evolution.

Laboratory tests showed that the best-performing compound—$[Cu(C_{6p})](PF_6)_7$—achieved a Faradaic efficiency of 86%. This means nearly nine out of ten electrons were used productively to make ammonia. This performance is among the highest reported for molecular copper catalysts operating in water at room temperature.

The process is the electrocatalytic nitrate reduction reaction. It involves passing an electrical current through a catalyst in a water-based system. Each nitrate ion (NO_3^-) accepts eight electrons and nine protons to become ammonia. The HKU team showed that by adjusting the number of positive charges and the tightness of the catenane rings, they could fine-tune the catalyst's interaction with different reaction steps. Tighter rings enhanced stability, while more charged groups improved selectivity for ammonia.

Experiments also revealed that the mechanical bond helped maintain the copper center's shape even during extended operation. Without this interlocking, typical copper complexes tend to decompose or convert into less active species. Copper can readily switch between +1 and +2 oxidation states during reactions, affecting catalyst performance. Therefore, confirming that the catalyst maintains Cu(I) is crucial. The team used Cu L-edge X-ray absorption spectroscopy (XAS), a soft X-ray technique, to examine the electronic structure and oxidation state of copper at **TLS 20A1**. The nearly identical spectra of $[Cu(C_{6p})](PF_6)_7$, its carbon-supported form, and the reference confirm that all species contain Cu(I) rather than Cu(II) (**Fig. 3**, see next page). These results demonstrate that the mechanical interlocking effectively stabilizes the Cu(I) environment, leading to the catalysts' high selectivity and durability.

This research represents an important step toward closing the nitrogen cycle, a key sustainability goal in environmental chemistry. The method can both purify water and produce green fertilizers using renewable electricity. Additionally, the concept of mechanical interlocking introduces a new approach to catalyst design. Structural engineering at the molecular

level can now achieve comparable performance with earth-abundant materials, reducing reliance on expensive metals such as platinum or palladium.

As Tse explained, the interlocked copper system "demonstrates that precision molecular design can solve long-standing challenges in catalysis—stability, selectivity, and efficiency—without relying on rare metals." The team plans to expand this approach to other catalytic reactions. They also aim to integrate their catalysts into scalable devices that could convert wastewater pollutants into useful resources on an industrial scale. According to Au-Yeung, "Mechanically interlocked ligands offer a powerful platform for tailoring catalysts at the molecular level. This work provides a blueprint for developing robust, efficient systems for sustainable chemical transformations."

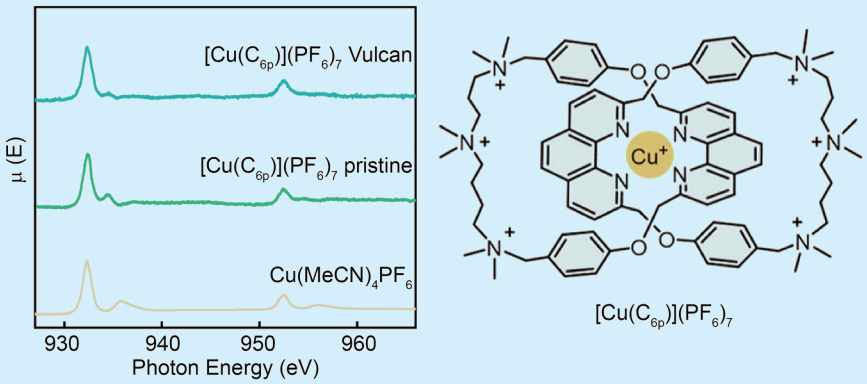


Fig. 3: Cu L_3-edge XAS of $Cu(MeCN)_4(PF_6)$ reference (orange), $[Cu(C_{6p})](PF_6)_7$ pristine (green), and $[Cu(C_{6p})](PF_6)_7$ supported on Vulcan (blue). XAS spectra were collected in total electron yield mode. [Reproduced from Ref. 1]

Through innovative molecular design, Au-Yeung and Tse's team at HKU transformed an environmental challenge into an opportunity for clean chemical production. Their copper catenane catalysts convert nitrate pollution into useful ammonia and demonstrate how mechanical chemistry can redefine the future of sustainable catalysis. (Reported by Shu-Chih Haw)

TLS 20A1

- Soft X-ray Absorption Spectroscopy
- Energy-related Materials, Catalytic Materials, Electron-correlated Materials, Molecular Films, Biomaterials

Reference

1. Y. Deng, X. Mo, S. K.-M. Lai, S.-C. Haw, H. Y. Au-Yeung, E. C. M. Tse, J. Am. Chem. Soc. **147**, 14316 (2025).

When Order Defies Nature: Hexagonal High-Entropy Nanocrystals for Accelerated Hydrogen Evolution

Atomic engineering characterized by in situ X-ray diffraction and X-ray absorption spectroscopy leads to the design of novel catalysts for hydrogen production.

In the world of nanoscience, order and chaos often coexist in strange harmony. Imagine arranging five precious metals—ruthenium (Ru), rhodium (Rh), palladium (Pd), platinum (Pt), and iridium (Ir)—into a single, nanosized crystal. Each atom competes for space, but they somehow settle into a balanced configuration, forming what scientists call a high-entropy alloy (HEA). These materials, composed of multiple metallic elements in nearly equal proportions, have attracted enormous interest because of their unusual stability, catalytic properties, and resistance to degradation. There are three key questions in this field. First, how do these atoms organize themselves at the smallest scales? Second, can they form unconventional structures that nature rarely favors? Third, what forces allow such structures to persist? These are the questions driving a recent study on $Ru@Ru_{0.2}Rh_{0.2}Pd_{0.2}Pt_{0.2}Ir_{0.2}$ core–shell nanocrystals, where Tung-Han Yang (National Tsing Hua University) and his collaborators engineered a new type of high-entropy material with a hexagonal close-packed (HCP) shell, a crystal structure that is normally unstable for this combination of elements. Through cutting-edge X-ray experiments, this study offers a rare glimpse into how atomic architecture evolves and stabilizes under extreme conditions.

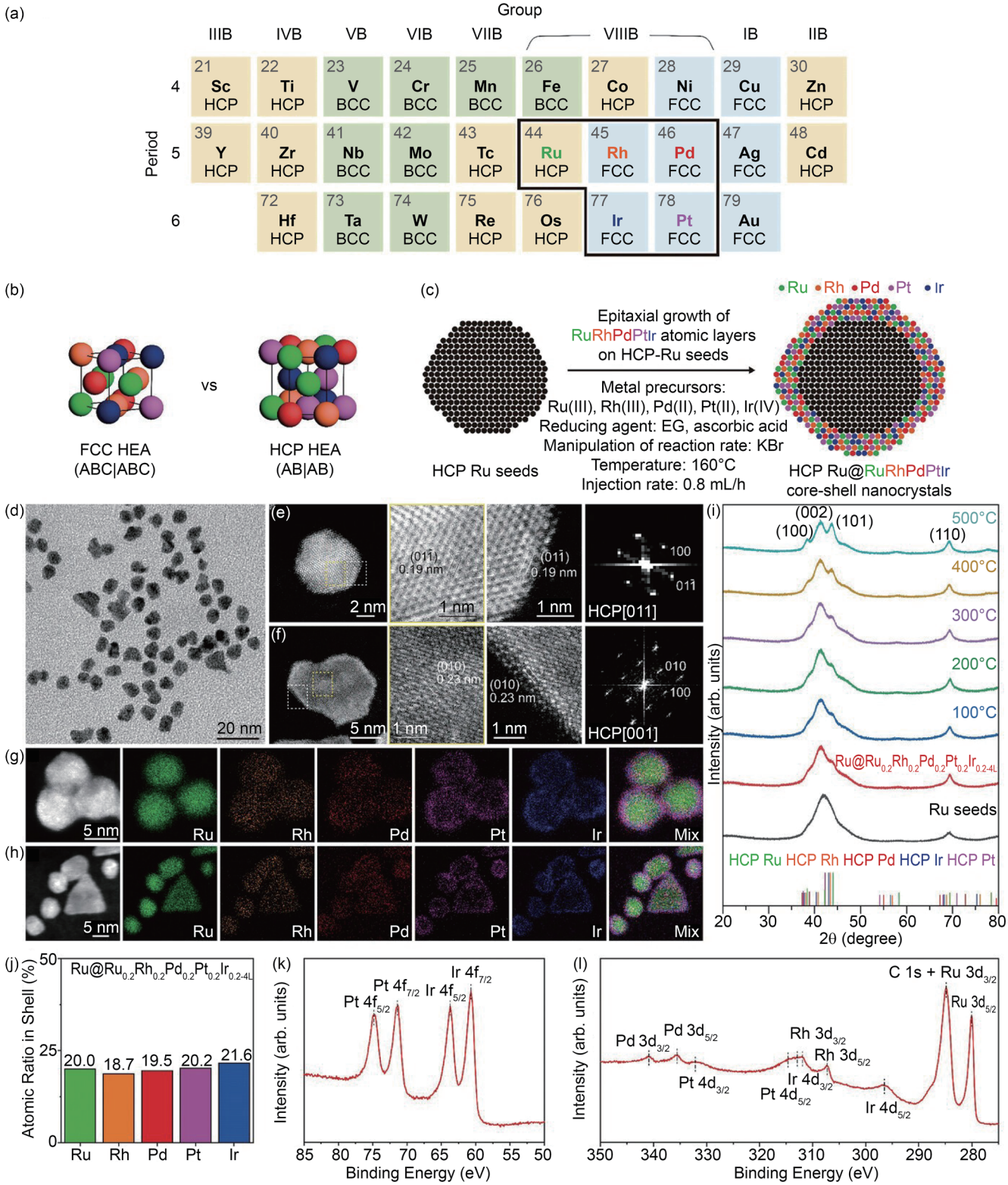


Fig. 1: Synthetic design and characterization of HCP Ru@RuRhPdPtIr core–shell nanocrystals. (a) The thermodynamically stable crystal structures of transition metals (HCP highlighted in orange, FCC highlighted in blue, and BCC highlighted in green). (b) The unit cells of FCC and HCP RuRhPdPtIr HEA. (c) Schematic of epitaxial growth to obtain HCP RuRhPdPtIr shells on Ru seeds. (d–h) TEM, HAADF-STEM, FFT, and EDS mapping analysis of $Ru@Ru_{0.2}Rh_{0.2}Pd_{0.2}Pt_{0.2}Ir_{0.2\text{-}4L}$ core–shell nanocrystals. (i) Synchrotron HRPXRD analysis of Ru seeds and $Ru@Ru_{0.2}Rh_{0.2}Pd_{0.2}Pt_{0.2}Ir_{0.2\text{-}4L}$ with *in situ* heating. (j) ICP-OES analysis of $Ru_{0.2}Rh_{0.2}Pd_{0.2}Pt_{0.2}Ir_{0.2\text{-}4L}$ shells. (k,l) XPS spectra of $Ru@Ru_{0.2}Rh_{0.2}Pd_{0.2}Pt_{0.2}Ir_{0.2\text{-}4L}$ in the regions of (k) 50–85 eV and (l) 275–350 eV. [Reproduced from Ref. 1]

A core of Ru acts as the seed, guiding the growth of a shell made from five noble metals, each of which has its own atomic preferences in crystal structures. In most metals, nature favors the FCC structure, where atoms pack in a symmetrical cube. However, under the right conditions, the researchers discovered that the Ru core can coax its metallic neighbors into adopting the HCP structure, yielding a hexagonal arrangement rarely observed in high-entropy alloys. The team confirmed this transformation using *in situ* high-resolution powder X-ray diffraction (HRPXRD) at the synchrotron facility **TPS 19A** in the NSRRC. Unlike conventional XRD, which provides a static snapshot, *in situ* measurements capture the structural evolution of materials in real time as it is heated or cooled.

The diffraction patterns are shown in **Fig. 1**. At room temperature, two new peaks appearing around 38.5° and 43.9° emerged once the RuRhPdPtIr shell formed, corresponding to the HCP (100) and (101) planes. These signals confirmed that the newly grown shell adopted the same hexagonal structure as its Ru core, forming a coherent epitaxial layer. In other words, the atoms lined up in perfect registry with the underlying Ru lattice. When the temperature increased, the diffraction peaks remained sharp and well-defined up to 500 °C, proving the exceptional thermal stability of this structure. The results suggested that even though the alloy combined five different elements, each of which having its own preferred crystal symmetry, the overall configuration resisted collapse into a more common FCC phase. The researchers estimated that the shell comprises roughly four atomic layers (~1.7 nm thick), an arrangement so thin and precise that it could only exist under the stabilizing influence of the Ru template.

However, this structural harmony has limits. The study found that when the HEA shell grows beyond six atomic layers, the atoms begin to rebel against the Ru template. *In situ* and *ex situ* imaging revealed that the smooth, epitaxial layers gave way to rough, island-like growth. Eventually, the hexagonal order gave way to the thermodynamically favored FCC structure—a more relaxed, cubic packing typical of bulk metals. This delicate balance between epitaxial templating and atomic self-preference reflects a universal tension in materials science: structure versus freedom. Thin layers can be forced into unnatural arrangements by the substrate beneath them, but as the material thickens, the internal strain relaxes, and the atoms revert to their preferred configurations. In this case, maintaining the exotic HCP form required precise control of growth kinetics, keeping the rate of atomic diffusion higher than that of deposition to ensure ordered layering.

To move beyond geometry and uncover the electronic personality of these materials, the researchers turned to synchrotron-based X-ray absorption spectroscopy (XAS), as summarized in **Fig. 2**. This technique goes far deeper than traditional imaging, and it reveals how atoms bond and share electrons, offering clues about the forces that hold the alloy together. Two complementary modes of XAS were used. The first, X-ray absorption near-edge structure (XANES), identifies the oxidation state and local electronic environment of each element. The second, extended X-ray absorption fine structure (EXAFS), measures how atoms are spaced and coordinated. This essentially mapped the hidden geometry of atomic neighborhoods. The XAS-related measurements were conducted at **TLS 01C1** and **TPS 44A** in the NSRRC.

Comparing the HCP Ru@$Ru_{0.2}Rh_{0.2}Pd_{0.2}Pt_{0.2}Ir_{0.2}$ structure with its FCC counterpart (Pd@$Ru_{0.2}Rh_{0.2}Pd_{0.2}Pt_{0.2}Ir_{0.2}$), the researchers observed striking differences. The valence state of Ir, for instance, followed a distinct order: metallic Ir^0 in pure foil < Ir in the FCC alloy < Ir in the HCP alloy < oxidized Ir^{4+} in IrO^2. This trend suggested that the hexagonal structure imposed a unique electronic environment, slightly oxidizing Ir compared to the FCC form. The EXAFS spectra further illuminated the atomic bonding within these alloys. For all five elements, alloy "doublet" peaks appeared between 1.8 and 2.7 Å. These are distinct signatures of interatomic bonding between different species. More importantly, the coordination numbers and bond lengths revealed subtle but meaningful differences: the Pt-Pt and Ir-Ir distances in the HCP phase (2.713 and 2.607 Å) were shorter than in their pure metallic foils (2.750 and 2.706 Å). This contraction hinted at stronger atomic interactions, likely due to the compressive strain imposed by the Ru core and the high degree of atomic mixing.

Electrochemical measurements revealed that the hexagonal high-entropy Ru@$Ru_{0.2}Rh_{0.2}Pd_{0.2}Pt_{0.2}Ir_{0.2}$ nanocrystals exhibit remarkable activity for the alkaline hydrogen evolution reaction. The catalyst required a significantly lower overpotential to reach 10 mA cm^{-2} and demonstrated a smaller Tafel slope compared to its FCC-phase counterpart, indicating faster reaction kinetics and more favorable electron transfer. This superior activity originates from the synergistic interplay of the five noble metals, whose compressed interatomic distances and modified electronic structure—confirmed by XAS—enhance both water dissociation and hydrogen adsorption. The HCP configuration exposes a greater number of unsaturated active sites and optimizes hydrogen binding energy, bridging the gap between sluggish water activation and hydrogen desorption steps. Moreover, long-term stability tests showed negligible degradation over extended operation, highlighting the robustness of the epitaxially stabilized HCP structure. Together, these features make the Ru-based high-entropy nanocrystal a powerful candidate for next-generation electrocatalysts in sustainable hydrogen production. (Reported by Dun-Yen Kang, National Taiwan University)

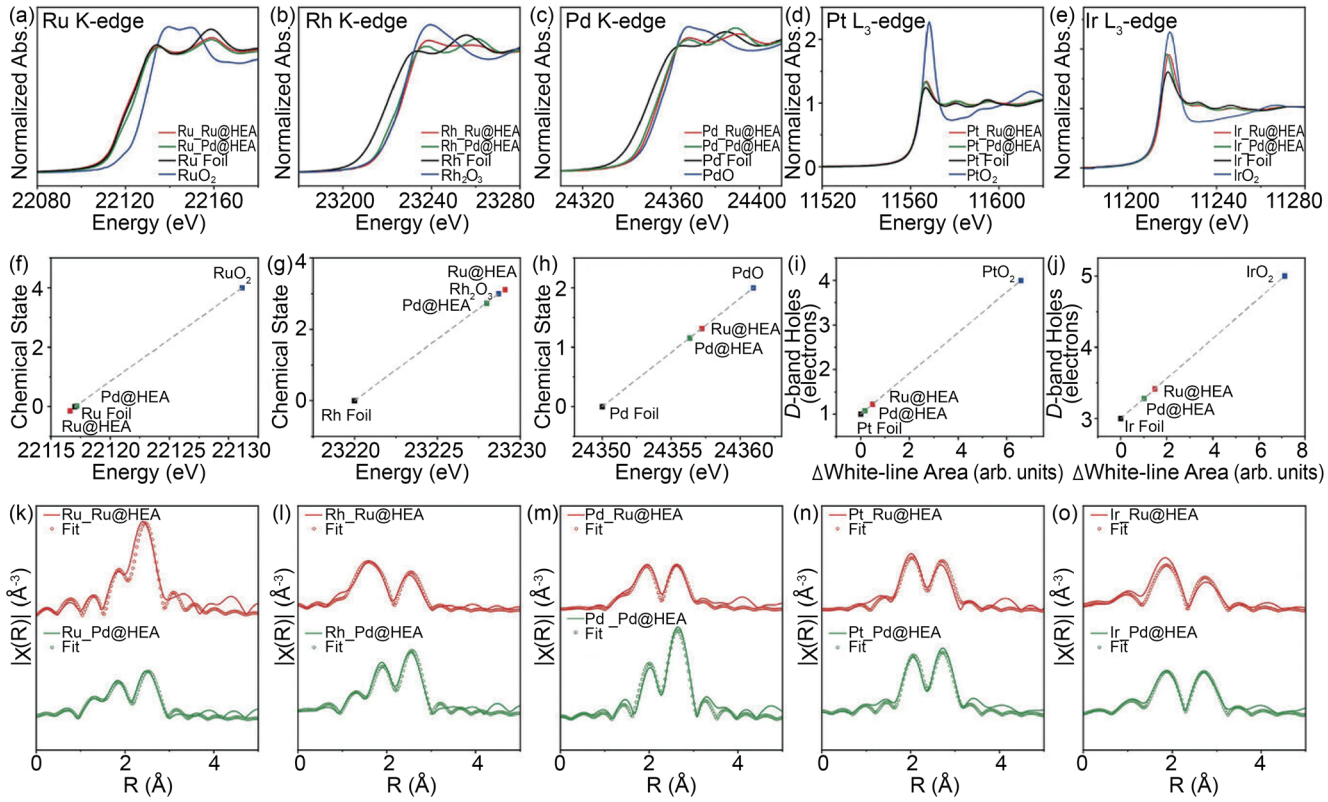


Fig. 2: Electronic structures and atomic coordination environments of HCP Ru@$Ru_{0.2}Rh_{0.2}Pd_{0.2}Pt_{0.2}Ir_{0.2\text{-}4L}$ and FCC Pd@$Ru_{0.2}Rh_{0.2}Pd_{0.2}Pt_{0.2}Ir_{0.2\text{-}4L}$ core–shell nanocrystals. (a–e) XANES spectra of HCP Ru@$Ru_{0.2}Rh_{0.2}Pd_{0.2}Pt_{0.2}Ir_{0.2\text{-}4L}$, FCC Pd@$Ru_{0.2}Rh_{0.2}Pd_{0.2}Pt_{0.2}Ir_{0.2\text{-}4L}$, and their corresponding metallic foils and oxidation states at the (a) Ru K-edge, (b) Rh K-edge, (c) Pd K-edge, (d) Pt L_3-edge, and (e) Ir L_3-edge. (f–j) Determination of chemical states and formal *d*-band hole count of Ru, Rh, Pd, Pt, and Ir elements for HCP Ru@$Ru_{0.2}Rh_{0.2}Pd_{0.2}Pt_{0.2}Ir_{0.2\text{-}4L}$ and FCC Pd@$Ru_{0.2}Rh_{0.2}Pd_{0.2}Pt_{0.2}Ir_{0.2\text{-}4L}$: (f–h) Absorption energy position versus chemical state of (f) Ru K-edge, (g) Rh K-edge, and (h) Pd K-edge; (i,j) White-line peak area difference versus formal *d*-band hole count of (i) Pt L_3-edge and (j) Ir L_3-edge. (k–o) FT-EXAFS spectra (lines) and curve fits (points) of HCP Ru@$Ru_{0.2}Rh_{0.2}Pd_{0.2}Pt_{0.2}Ir_{0.2\text{-}4L}$ and FCC Pd@$Ru_{0.2}Rh_{0.2}Pd_{0.2}Pt_{0.2}Ir_{0.2\text{-}4L}$ at the (k) Ru K-edge, (l) Rh K-edge, (m) Pd K-edge, (n) Pt L_3-edge, and (o) Ir L_3-edge. The data are k^2-weighted and without phase correction. [Reproduced from Ref. 1]

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TPS 19A High-resolution Powder X-ray Diffraction
TPS 44A Quick-scanning X-ray Absorption Spectroscopy
TLS 01C1 EXAFS

- HRPXRD, XAS, XANES
- High-entropy Alloy, Hydrogen Evolution Reaction, Hexagonal Close-packed Structure

Reference

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